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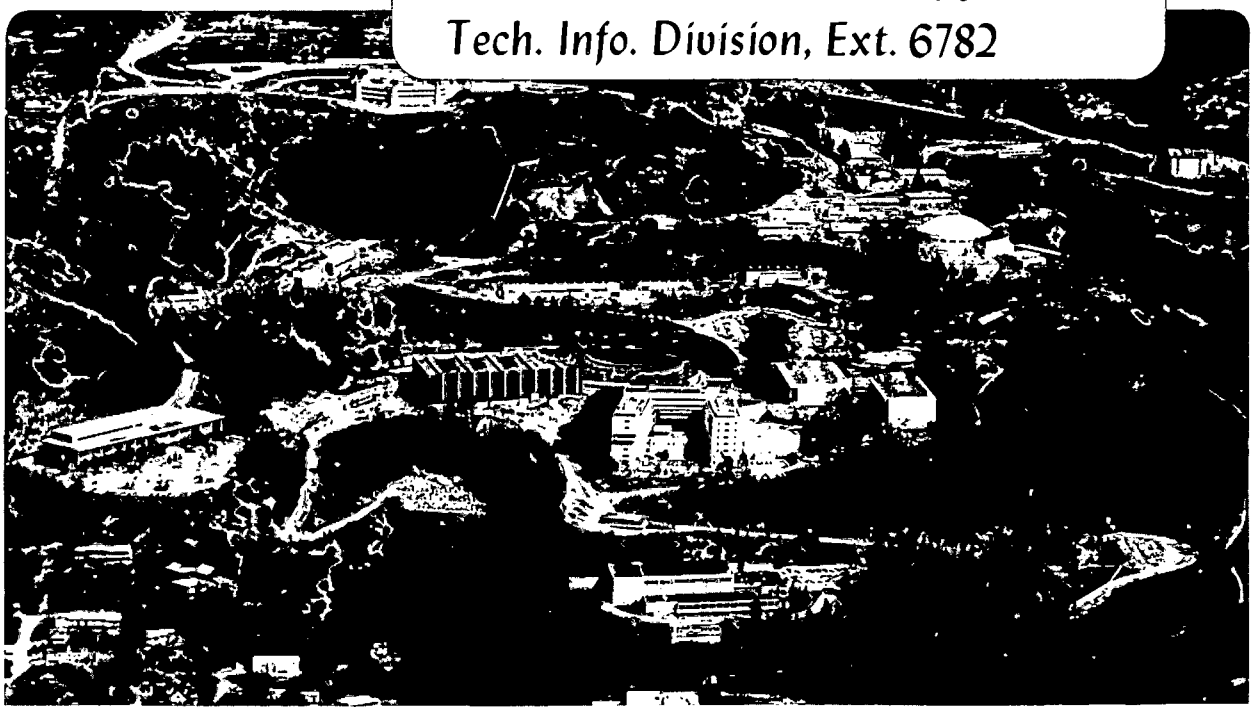
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B.H. O'Connor and J. M. Jaklevic

May 1980

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ABSTRACT

Direct x-ray powder diffraction analysis of airborne particulate material collected in the St. Louis area on cellulose ester membrane filters has given results for both fine and coarse particle fractions which are consistent with elemental data, and which are also in keeping with expectations based on the anthropogenic and natural sources of particulates in the area. The most frequently observed compounds in the fine fraction samples were $(NH_4)_2SO_4$ and the double salts $(NH_4)_2SO_4.PbSO_4$ and $3(NH_4)_2SO_4.H_2SO_4$. The occurrence of $(NH_4)_2SO_4.PbSO_4$ appears to be mainly associated with discrete source activity although the formation of this compound by the interaction of automotive PbBrCl with atmospheric $(NH_4)_2SO_4$ cannot be ruled out. The minerals calcite ($CaCO_3$) and α-quartz (SiO_2) are present as major components in almost all coarse fraction samples as expected from the composition of surface rocks in the region. Some coarse fraction samples also contain compounds apparently emitted by nearby industrial sources.

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INTRODUCTION

We report the results of a study of ambient aerosol samples using x-ray powder diffraction (XPD) to characterize the chemical forms of major constituents. The samples examined by XPD were selected from a library of 35,000 samples collected with dichotomous air filter instruments stationed at ten sites in the St. Louis metropolitan area. The samples had been analyzed by beta-ray attenuation and x-ray fluorescence spectrometry (Jaklevic et al, 1976; Loo et al, 1978; Goulding et al, 1978).

There are few reports in the literature of XPD studies of airborne particulates, due mainly to the relatively low sensitivity of conventional XPD procedures. Brosset et al (1975) used the XPD Guinier photographic method to identify various sulfur compounds in particulate material which had been scraped from air filters and remounted in a form suitable for analysis. In another study, Davis et al (1977, 1978) employed x-ray powder diffractometry (XPDFT) to analyze mineral phases collected on glass fiber filters by HI-VOL sampling. This avoided potential problems associated with sample preparation since XPDFT can be performed on the filter without disturbing the sample.

The present study also employed XPDFT, permitting direct analysis of the aerosol material on the filter medium. Also,the use of membrane filters for sample deposition gave a substantial gain in signal to noise, compared with that obtained using glass fiber filters. A further improvement resulted from the acquisition of filtered material by dichotomous sampling whereby the fine and coarse particle size fractions of the bimodal particle size distribution observed in urban air samples are collected separately. Dichotomous sampling results in the deposition of material mainly of geological origin on the course fraction filter, and nearly all the anthropogenic material on the fine fraction filter. Accordingly, the diffraction patterns were reduced in complexity and more readily interpreted.

Although, the main objective of the investigation was to determine profiles of chemical compounds constituting the particulate component of the atmosphere above an urban area, the samples selected for XPDFT analysis were biased in favor of heavy aerosol depositions to enhance signal strength. Therefore the compounds observed in some of the samples do not reflect typical

urban ambient aerosol conditions but rather chemical activity associated with air pollution episodes.

Of special interest regarding the fine fraction samples is the nature of the sulfur and lead compounds which normally originate from fossil fuel combustion and from spark ignition engines, respectively. Also of interest are the chemical forms of particulates of geological origin and the relationship of these to the geochemistry of the surrounding region.

BACKGROUND

The chemical properties of tropospheric sulfur aerosols were reviewed recently by Charlson et al (1978). The observed sulfur compounds are mainly of oxidation state +6 and belong to the phase system H_2SO_4/NH_3. The limited data available in the literature indicate that $(NH_4)_2SO_4$, with the crystal structure of the mineral mascagnite, is the most common crystalline phase in aged high-sulphur aerosols with a high abundance of NH_3. Additional crystalline sulfates observed are two binary ammonium acid sulfate compounds of the type $x(NH_4)_2SO_4.yH_2SO_4$, which form when insufficient NH_3 is present to fully neutralize the H_2SO_4. The compound $(NH_4)_2SO_4.H_2SO_4$ is difficult to detect by XPD methods as it deliquesces at a relative humidity of 30 to 40 percent and therefore mainly occurs as a liquid droplet aerosol. The second binary acid sulfate which has been observed in other XPD studies is $3(NH_4)_2SO_4.H_2SO_4$ in the structural form of the mineral letovicite which, according to the review of Charlson et al, is found less frequently than $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.H_2SO_4$.

The chemical nature of automotive lead particulate emissions, and their subsequent reaction pathways in the atmosphere, has been the subject of several investigations (Hirchler et al, 1957, 1964; Habibi, 1973; Ganley and Springer, 1974). Crystalline lead bromochloride, PbBrCl, is the lead compound of highest concentration in auto exhaust when the fuel additive TEL-CB (comprising a mixture of the octane-boosting compound, tetraethyl lead, and the scavenging agents, ethylene dichloride and ethylene dibromide) is employed. Substantial evidence suggests that, in addition to the expelled PbBrCl, the

double salts $2NH_4Cl.PbBrCl$, α- and β-$NH_4Cl.2PbBrCl$ condense in the volume immediately beyond the tailpipe during the cooling and mixing of exhaust in air. The fate of these compounds as the aerosol ages is the subject of contention. Ter Haar and Bayard (1971) claimed that the halide compounds rapidly decompose to form lead carbonates, oxycarbonate, and oxides, based on electron microprobe x-ray analysis of freshly emitted and aged aerosol. However, there is some doubt about the validity of these interpretations following a critique of the Ter Haar-Bayard study by Heidel and Desborough (1975). A recent investigation has pointed to the interaction of lead and sulfur compounds as being of primary importance in the aging of urban aerosols. Biggins and Harrison (1979), subsequently designated B and H, have used photographic XPD to identify the salt $(NH_4)_2SO_4.PbSO_4$ as the major lead compound in almost all air filter samples collected at a series of widely separated sites in England. Also observed by B and H, but less frequently, were $PbSO_4$, PbBrCl and PbBrCl. $(NH_4)_2BrCl$. The atmospheric observations were supported by reaction chamber experiments whereby it was proposed that $(NH_4)_2SO_4.PbSO_4$ forms by reaction between PbBrCl and $(NH_4)_2SO_4$ droplets following coagulation.

In addition to automotive Pb sources, the present study also identified sources associated with specific episodes during which selected elements would be elevated to several times their normal concentrations for a short period of time. These elements include Pb,Cu,Zn,Cl,Cd and others. The identity of the sources responsible for the episodes is speculative at present and the chemical forms of the source elements are largely unknown.

The coarse particle samples in the St. Louis aerosol are known from elemental analyses to correlate with the composition of rocks and soils in the surrounding area. The surface rocks and soils within a nominal 50-mile radius of St. Louis are essentially sedimentary with the following rocks predominating: limestone, dolomite, sandstone, shale, and various clays (State of Missouri Geological Survey and Water Resources, 1967). Accordingly the mineral compounds likely to be encountered in coarse fraction aerosol samples are calcite ($CaCO_3$) from limestone, dolomite ($CaMg(CO_3)_2$), α-quartz (SiO_2) from sandstone and shale, illite (a major constituent of shale), and clay minerals.

DATA ACQUISITION

The filter samples investigated by XPDFT were collected during the St. Louis Regional Air Pollution study with dichotomous samplers operated continuously at 50 ℓ/min over periods of 6 or 12 hours. The samples consisted of fine (2.4 μm aerodynamic diameter) and course (2.4-20 μm) particles deposited on pairs of 1.2 μm pore size cellulose ester membrane filters (Millipore* type RAWP) of effective diameter 32 mm and an average tare of ∿4 mg/cm^2.

The samples were from stations 103 and 105 (inner city sites), 118 (suburban, 16 km south of St. Louis downtown) and 124 (rural, 38.5 km south of St. Louis downtown), along a line running in a southerly direction from the city. (See Loo, et al 1978 for a complete description of sites.) It was found that filter loadings in excess of 100 μg/cm^2 yielded useful diffraction patterns for the XPDFT conditions employed. For each station, six fine and six course fraction samples were examined. Sample collection conditions, their mass loadings, and elemental concentrations are detailed in Tables 1 and 2 for the fine and coarse samples, respectively.

Complete details of the data measurement procedures are given by O'Connor and Jaklevic (1979), the information therein being summarized in the following paragraphs.

The XPDFT measurements were performed with a conventional Norelco Bragg-Brentano* diffractometer fitted with a Cu anode x-ray tube operating at 40 kV and 20 mA. The incident beam was monochromatized with an 8.4 μm Ni filter and the diffracted beam was monitored with a Xe side-window proportional detector arm. The goniometer was stepped in increments of 0.04° in 2θ from 10° to 50°, corresponding to the d-spacing range 8.9Å--1.82Å. A 1° divergence slit was employed with a matching anti-scatter slit and a 0.05° receiving slit.

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*Reference to a company name or product name does not imply approval or recommendation of the product by the University of California or the United States Department of Energy to the exclusion of others that may be suitable.

Scans were acquired over 23-hour periods. Even with this long collection time, the scans are of relatively poor quality compared to those normally obtained in XPDFT of infinitely thick samples. The counting rates of the diffraction lines are very low and this problem is compounded by an unfavorable signal to noise ratio caused by background radiation scattered from the filter substrate.

The diffraction patterns were reduced to sets of peak positions and relative intensities above background for the subsequent search/match phase identification process. Figures 1 and 2 show a representative set of the reduced data in bar graph form for the fine and coarse fraction samples respectively. The examples shown are the patterns for Station 103. The data for all stations are contained in a LBL internal report (O'Connor and Jaklevic, 1979b).

The relative amounts of a given compound in the samples examined were found by assuming a linear relationship between line intensity and compound concentration. The assumption is reasonable as the mass loadings for all samples are below commonly accepted limits above which the intensities are biased by attenuation effects.

RESULTS

The data were interpreted by two strategies. In the first, the diffractograms for the six patterns in a given particle size category and for a particular recording station were displayed together as shown in Figures 1 and 2. In this way the lines associated with the most frequently occurring major crystalline phases were obvious. These common lines were then used to identify the major components by means of a manual Hanawalt search per match procedure which highlights probable solutions from the Joint Committee on Powder Diffraction Standards (JCPDS) set of diffraction patterns for some 25,000 inorganic compounds. Examples of the excellent correlation between the observed and the chosen reference patterns are shown in Figure 3. For both the manual and the subsequent automated search/match identification process, elemental concentrations were used to eliminate solutions which are

acceptable on the basis of the diffraction data but unreasonable on chemical grounds. The elemental concentrations, measured by energy dispersive x-ray spectrometry (Jaklevic et al, 1976), were those for Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Cd, Sn, Sb, Ba, Hg and Pb.

Following identification of the commonly occurring phases, patterns with additional lines were examined by a second strategy. The patterns of these samples were analyzed by the Powder Diffraction Search/ Match (PDSM) automated system which is a commercial service operated by the Interactive Sciences Corporation through the Telenet computer network. The PDSM package bases its search on the fifteen strongest lines for each entry in the JCPDS file of diffraction patterns, and reduces the 25,000 contenders to a short list of possible solutions. This is achieved by rejecting patterns first on chemical grounds, and subsequently through mismatching between observed and reference patterns according to the precision in measuring line position and intensity. The pattern interpretations are presented in Tables 3 and 4. Components classified as being assigned with high probability are those with an acceptable match for the four strongest lines of the standard pattern. Those designated "assignment less certain" match only two or three strong lines. Various aspects of the results are discussed in the remainder of this section.

Fine Fraction Samples

Station 103

The major component phases for this suite of samples are $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.PbSO_4$ in varying proportions. $(NH_4)_2SO_4.PbSO_4$ is observed in all six samples and $(NH_4)_2SO_4$ in four. The unusually high Pb and Zn concentrations and anomalous Pb/Br ratios for several of these samples indicate the probable existence of a discrete source of fine particulates in addition to the normal automotive Pb and fossil fuels. Only the second sample (103-2) can be regarded as being predominantly vehicular in origin. This is based both on the systematics of elemental concentrations before and after this sample interval and on the Pb/Br ratio (4.9) which is typical for an aged automotive aerosol.

The chemical species in all cases are predominantly influenced by the presence of atmospheric sulphate compounds. The persistent occurence of $(NH_4)_2SO_4 . PbSO_4$ is in agreement with the results of B and H for the case of automotive Pb sources. However, since much of the Pb observed in the present study presumably has different origins, some additional reaction is probably involved. It should also be stressed that some caution should be exercised in attributing the formation of $(NH_4)_2SO_4 . PbSO_4$ to atmospheric processes as it is possible that the compound forms on the filter deposit following collection.

The mechanism proposed by B and H for the formation of $(NH_4)_2SO_4 . PbSO_4$ is:

$$2\ PbBrCl + 2\ (NH_4)_2SO_4 \rightarrow (NH_4)_2SO_4 . PbSO_4 + PbBrCl . (NH_4)_2BrCl .$$

The S/Pb ratio for all six samples exceeds the value 0.31 which is the stochastic value for $(NH_4)_2SO_4 . PbSO_4$, and is a necessary condition for complete conversion to the double sulphate. It is therefore conceivable that the Pb in all six samples is mainly in the form of $(NH_4)_2\ SO_4 . PbSO_4$ which has formed by the reaction of all of the originally present PbBrCl or other Pb compounds with an excess of $(NH_4)_2SO_4$. The observation of $(NH_4)_2SO_4$ in four of the samples is consistent with this supposition. If the above reaction is the means whereby $(NH_4)_2SO_4 . PbSO_4$ forms, the salt $PbBrCl . (NH_4)BrCl$ must be present below the limit of detection or have undergone further reaction.

Lead halide compounds, in particular PbBrCl, were not observed even though substantial amounts of Cl and/or Br are present in some of the samples. Given the stoichiometric Pb/Cl and Pb/Br ratios for PbBrCl (5.8 and 2.6, respectively), it is conceivable that PbBrCl is present in significant amounts in at least two samples but below the XPDFT limit of detection for this compound. Alternatively, PbBrCl or other Br- and Cl-containing compounds could be present in amorphous form and therefore undetectable by XPDFT.

The sample with the highest Zn level (103-1) contains the hydrated double salt $(NH_4)_2SO_4 . ZnSO_4 . 6H_2O$ as a major component. This conclusion is strongly supported by extended x-ray absorption spectroscopy (EXAFS) analysis in the vicinity of the Zn absorption edge (Jaklevic et al, 1979). The second highest Zn level (103-4) also appears to contain the Zn double salt on the basis of our diffraction measurements and the EXAFS analysis. The compound has also been observed by B and H (1979b).

Station 105

Strong diffraction patterns were observed for four of the six samples, these having high S concentrations (21-36 $\mu g/cm^2$) and $(NH_4)_2SO_4$ as a major component. In the two samples with relatively high Pb and S concentrations (105-3 and 105-6), $(NH_4)_2SO_4.PbSO_4$ is also a major component which is consistent with the findings for Station 103. The double salt is possibly present in 105-1 just above the limit of detection, and, if present in the remaining high S sample (105-5), must be below the limit. It appears that the detection limits for $(NH_4)_2SO_4.PbSO_4$ in terms of Pb and S levels are about 3 and 0.5 $\mu g/cm^2$, respectively, when expressed as Pb or S levels.

The patterns for 105-2 and 105-4 are very weak with insufficient line definition for interpretation. The Pb levels for these samples (9.5 and 13.2 $\mu g/cm^2$) substantially exceed the limit of detection specified in the preceding paragraph for $(NH_4)_2SO_4.PbSO_4$, and therefore we conclude that the Pb is not in the double salt form. Although $(NH_4)_2SO_4$ lines were not observed, the S may still be present in that form as the detection limit for the compound according to the Station 103 results is in the vicinity of 10 $\mu g/cm^2$ of S as $(NH_4)_2SO_4$. The Pb/Br ratio for these samples are close to the stoichiometric value for PbBrCl and would argue strongly for the Pb concentration being totally associated with that specific chemical form. This interpretation is supported by the observed Pb and Br concentrations for samples acquired in adjacent time periods. The evidence suggests that these particular samples represent isolated peaks of fresh automotive generated aerosol. The lack of an observable PbBrCl diffraction pattern even at these elevated concentrations supports the conclusion that the PbBrCl is present but in a physical form which is undetectable by the present XPDFT measurements.

Station 118

$(NH_4)_2SO_4$ is again observed, this time as a contributor to five of the six diffraction patterns. As was previously observed, for Stations 103 and 105, there is a strong tendency for $(NH_4)_2SO_4.PbSO_4$ lines to appear when there are several $\mu g/cm^2$ of Pb and sufficient S for conversion. The compound $3(NH_4)_2SO_4.H_2SO_4$ (see Introduction), which was not detected in the Station 103 and 105 samples, is a major phase in three of the samples.

Sample 118-4 has a pronounced line doublet and additional weaker lines which, together with the observed concentrations for Al, Si, and Ca, indicate that the silicate mineral gismondine, $Ca(Al_2Si_2O_8).4H_2O$, may be present. Alternatively, the mineral α-quartz may be present since its most prominent lines coincide with those for gismondine. As gismondine is not found in surface soils and rocks in the St. Louis area, the compound probably originates from an anthropogenic source if present. The alternative choice, α-quartz, seems unlikely as the mineral occurs frequently in the course fraction samples but not in any of the other fine fraction samples.

Station 124

The acidic phase $3(NH_4)_2SO_4.H_2SO_4$ is the most frequently occurring major compound being found in three samples. $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.PbSO_4$ are each present as major constituents in one sample, and there is evidence that the double Pb salt is present in a second sample.

The two samples with the highest Pb levels both contain $PbSO_4$ as well as $(NH_4)_2SO_4.PbSO_4$. The former has been observed by Olson and Skogerboe (1975) as the major lead compound in soils adjacent to freeways. However, in this study, the $PbSO_4$ may well orignate from non-vehicular sources. We also note that the observation of $PbSO_4$ at the outermost station may only occur because local non-vehicular sources in the vicinity of Station 124 differ markedly in nature from those near the inner stations.

Coarse Fraction Samples

Interpretation of the coarse fraction diffraction patterns is complicated by the difficulty that the most intense peaks of some plausible mineral compounds fall below the miniumum 2θ value for the patterns. In particular, the main peaks for some of the phyllosilicates (illite, biotite, montmorillonite) could not be determined.

Station 103

The main features of the diffraction patterns for the minerals α-quartz and calcite are found in all six measured patterns. This is consistent with the presence of sandstone, shale, and limestone in surface layers of the earth's crust in the vicinity of St. Louis.

The compounds $(0.7\ NH_4\ H_2PO_4).(0.4\ KH_2PO_4)$ and $(NH_4)_2SO_4$ account for the relatively high levels of P and K in 103-2 and S in 103-5, respectively. The probable source of these compounds is a fertilizer plant located 300 m to the northeast of the samplers.

Station 105

The mineral phases α-quartz and calcite are again observed in all samples, and one sample appears to contain the mineral dolomite. There are also pronounced features of the diffraction patterns of halite (NaCl) and zincite (ZnO) in samples 105-2 and 105-5, respectively, which coincide with relatively high elemental concentrations for Cl and Zn. Both compounds probably come from anthropogenic sources.

Stations 118 and 124

The persistent occurrence of α-quartz and calcite found in the Station 103 and 105 samples is again observed. The fact that these stations are more remote from industrial activity accounts for the relative lack of additional compounds not associated with soil dust.

Inter-Station Correlations

One particular sampling period (1976/233/00) is comprehensively covered in the diffraction data set. Samples are available for each site and size range with the exception of the coarse particle fraction for Station 105. The data are summarized in Table 5 which is abstracted from the earlier tables to facilitate comparison among sites.

This particular sampling period coincided with an episode during which the particulate elemental sulfur concentration was above 6 $\mu g/m^3$ for several days and was relatively uniform over the 50 km radius around St. Louis. Various elements had high concentrations during this six-hour interval particularly at the urban sites 103 and 105. These include Pb,Cl,Zn,Cu,Cd in the fine fraction and Ca,Fe,Pb and Si in the coarse fraction. The elemental concentrations at the suburban and rural sites, 118 and 124, exhibit no dramatic increases with the possible exception of Ca and Fe at site 118.

The powder diffraction analysis indicates the predominance of α-quartz and calcite in the coarse fraction samples for all sites. In the fine fraction, $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.PbSO_4$ are observed at the urban sites whereas $3(NH_4)_2SO_4.H_2SO_4$ is the dominant component at the rural sites. The difference in chemical form between the particulates associated with the background aerosol at the rural sites and the particles collected in the urban site would indicate that some transformations are being induced by the local source activity near the urban sites.

CONCLUSION

It has been shown that conventional powder diffraction methods can be applied to the qualitative measurement of chemical species collected from the ambient aerosol using dichotomous samplers. The observed diffraction pattern interpretations are consistent with the XRF elemental measurements. Also, the advantage of using dichotomous samplers is demonstrated by the obvious differences in chemical form between the fine and coarse particulate fractions--the fine fraction samples being predominantly combinations of sulfate and ammonium sulfate species whereas the course fractions are mainly α-quartz and calcite.

Since the samples were chosen for analysis on the basis of interesting elemental profiles, it is difficult to generalize the results in terms of typical urban atmospheric chemistry. Also, we cannot eliminate the possibility that many of the chemical effects (most notably the formation of lead and zinc ammonium sulfate) can occur on the filter after collection of the particles either by interaction with the other particulates or with gaseous species.

In order to apply XPDFT to the quantitative study of air particulates, several problems must be addressed. The question of transformations of compounds after collection on the filter needs to be studied as a matter of high priority. Also the lack of observable diffraction peaks from PbBrCl appears to indicate relatively low sensitivity for this and possibly other compounds. Insofar as low sensitivity might also arise from particle size effects, additional research is required on diffraction line broadening. Finally, one hopes that it is possible to relate the concentration of the observed compound to the intensity of the observed patterns in order to quantitatively measure the compound present. This would require the preparation of appropriate compound standards in physical forms which duplicate the urban aerosol. The quantitative determination of chemical compounds taken in conjunction with the measured elemental concentrations would then represent an important step in the characterization of ambient aerosol particulates.

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FIGURE CAPTIONS

Fig. 1 Diffraction patterns in bar graph form for the Station 103 fine fraction samples. Line assignments correspond to the interpretations in Table 3.

Fig. 2 Diffraction patterns in bar graph form for the Station 103 coarse fraction samples. Line assignments correspond to the interpretations in Table 4.

Fig. 3 Examples of the correlations between the observed patterns and the JCPDS patterns for $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.PbSO_4$.

TABLES

Table 1. Fine fraction sample elemental concentrations. Sample intervals at stations 103 and 105 were 6 hours, 118 and 124 were 12 hours.

Table 2. Coarse fraction sample elemental concentrations. Sample intervals at stations 103 and 105 were 6 hours, 118 and 124 were 12 hours.

Table 3. Results of XRDFT pattern interpretation for fine fraction samples.

Table 4. Results of XRDFT pattern interpretation for coarse fraction samples.

Table 5. Concentrations of important elements (ng/m^3) and XPDFT results for simultaneous samples at four sites for the interval 1976/233/00. The coarse particle results for site 105 are not available. An asterisk (*) indicates that the element is strongly peaked in this area.

Table 1. Fine fraction sample elemental concentrations. Sample intervals at stations 103 and 105 were 6 hours, 118 and 124 were 12 hours.

STATION	START TIME YEAR/DAY/HOUR	MASS $\mu g/cm^2$	MAJOR ELEMENTS ($\mu g/cm^2$) S	Cl	Fe	Br	Pb	Pb/Br	OTHER SIGNIFICANT ELEMENTS ($\mu g/cm^2$)
103-1	75/277/06	161	17.9	1.5	0.8	1.0	7.4	7.3	Zn = 6.5
103-2	76/160/18	250	33.4	1.4	1.3	0.8	3.9	5.1	
103-3	76/275/18	221	11.7	3.3	4.2	3.2	12.6	4.0	Ca = 2.2
103-4	77/008/06	199	31.2	0.2	3.3	0.5	3.8	8.0	Zn = 4.5, Cu = 0.5
103-5	76/174/00	117	8.2	2.7	1.1	0.5	3.2	6.1	Zn = 2.1, Cu = 0.6
103-6	76/233/00	148	19.9	1.3	1.3	0.6	9.3	15.5	
105-1	75/184/18	232	35.6	0.2	0.6	0.7	3.5	5.1	
105-2	75/265/06	73	4.2	1.2	0.2	4.4	9.5	2.2	
105-3	75/280/06	230	21.4	0.8	1.1	0.8	7.4	9.3	Zn = 2.4, Cu = 3.1
105-4	76/023/18	97	4.2	3.6	1.1	5.5	13.2	2.4	
105-5	76/154/00	144	24.3	0.7	1.1	0.2	1.1	6.5	Zn = 0.8
106-6	76/233/00	219	24.8	4.5	1.3	0.3	28.4	92.1	Zn = 1.3, Cu = 2.1
118-1	75/265/12	164	17.7	1.8	3.1	1.1	6.1	5.6	Zn = 2.3, Al = 12.4
118-2	76/121/00	120	12.4	-	0.5	0.3	10.1	31.0	Zn = 1.9
118-3	76/160/12	354	48.3	1.0	2.7	0.1	1.6	13.3	Si = 11.5, Ca = 5.8
118-4	76/162/00	332	57.5	-	1.3	0.1	2.9	38.0	Ca = 2.2
118-5	76/233/00	234	44.2	0.8	0.9	0.2	1.3	7.3	
118-6	76/261/12	93	16.4	0.2	0.3	1.9	6.1	3.2	
124-1	75/260/12	173	24.8	0.3	0.8	0.1	5.0		
124-2	75/269/00	124	12.4	2.4	1.1	0.4	19.1	49.0	Zn = 5.8
124-3	76/022/00	128	8.0	1.2	0.3	0.1	14.3	119	Cd = 0.1
124-4	76/160/00	164	26.1	0.3	0.6	0.1	2.3	21.0	Cd = 0.1
124-5	76/161/00	151	29.7	0.3	0.6	0.1	1.6	22.0	Cd = 0.1
124-6	76/233/00	195	37.2	0.6	0.7	0.2	0.8	5.0	

Table 2. Coarse fraction sample elemental concentrations. Sample intervals at stations 103 and 105 were 6 hours, 118 and 124 were 12 hours.

STATION	START TIME YEAR/DAY/HOUR	MASS $\mu g/cm^2$	MAJOR ELEMENTS ($\mu g/cm^2$) Al	Si	Cl	K	Ca	Fe	OTHER SIGNIFICANT ELEMENTS ($\mu g/cm^2$)
103-1	76/160/18	290	6.2		3.6	5.7	25.0	11.9	
103-2	76/174/00	340	5.5	21.9	8.4	13.9	28.1	16.6	P = 27.5
103-3	76/233/00	166	6.2	21.6	1.8	1.5	17.9	15.0	
103-4	76/261/18	234	8.2		1.9	2.9	34.7	12.8	
103-5	76/275/18	429	4.6		3.8	20.3	31.2	12.2	S = 41.3
103-6	76/275/18	360	9.7		3.4	6.2	40.7	27.8	
105-1	75/184/18								
105-2	76/184/18	141	3.1	11.7	11.5	1.1	16.6	3.8	
105-3	76/121/06	133	3.3	16.1	1.0	1.3	13.7	11.3	
105-4	76/238/00	219	5.3	16.6	1.5	1.5	18.3	12.8	Ti = 12
105-5	76/244/18	181	6.0	19.2	2.4	1.5	12.6	4.9	Zn = 43
105-6	76/275/18	336	8.0		1.0	3.1	42.9	15.5	Ti = 3.5
118-1	75/290/00	186		17.7			10.2	2.7	
118-2	76/233/00	213	8.0	20.4	1.5	2.2	35.9	5.8	
118-3	76/261/12	164	5.3	20.8	0.9	2.0	17.7	4.9	
118-4	76/265/12	115	4.0	17.7	0.6	1.8	14.6	3.5	
118-5	76/289/00	199	9.3	43.0	0.1	3.5	11.1	7.1	
118-6	77/008/12	71	3.1	7.5	4.9	0.6	3.5	2.2	
124-1	75/245/12	204	20.4	27.9	1.0	3.5	μ	5.3	
124-2	75/273/00	106		35.9	1.6	2.6	μ	3.1	
124-3	76/098/00	168	8.0	33.7		2.7	15.0	4.9	
124-4	76/133/12	239	12.0		0.2	4.0	21.7	7.1	
124-5	76/147/00	155	6.6	29.7	0.3	2.2	14.2	4.0	
124-6	76/233/00	111	7.1	16.4	0.3	1.8	6.2	4.4	

Table 3. Results of XRDFT pattern interpretation for fine fraction samples.

Station	Phases Contributing to Pattern				No. of Lines	
					Total	Unassigned
	AS	ASH	ALS	AZS		
103-1	X		X	X	21	3
103-2	X		X		18	1
103-3			X		10	-
103-4	X		X	0	16	-
103-5			X		4	-
103-6	X		X		18	-
105-1	X				19	2
105-2	very weak pattern					-
105-3	X		X		17	1
105-4	very weak pattern					-
105-5	X				14	-
105-6	X		X		26	4
				CAS		
118-1	X		X		16	-
118-2	X		X		20	3
118-3	0	X			19	1
118-4	X	X		0	26	1
118-5		X			15	2
118-6	X				13	1
				LS		
124-1	X				14	1
124-2			X	X	15	3
124-3			0	X	7	-
124-4		X			11	1
124-5		X			10	1
124-6		X			17	5

X = Assigned with high probability
0 = Assignment less certain

AS = $(NH_4)_2SO_4$

ASH = $3(NH_4)_2SO_4.H_2SO_4$

ALS = $(NH_4)_2SO_4.PbSO_4$

AZS = $(NH_4)_2SO_4.ZnSO_4.6H_2O$

LS = $PbSO_4$

CAS = $Ca\ Al_2Si_2O_8.4H_2O$

Table 4. Results of XRDFT pattern interpretation for coarse fraction samples.

Station	Phases Contributing to Pattern					No. of Lines	
						Total	Unassigned
	Q	C	KAP	AS			
103-1	0	X				16	9
103-2	0	0	X			13	5
103-3	0	0				4	1
103-4	X	X				10	2
103-5	0	0		X		18	4
103-6	0	X				12	3
			H	Z	D		
105-1	X	0				7	2
105-2	0	X	0			10	1
105-3	0	0				7	3
105-4	0	0				6	3
105-5	0	0		X		7	-
105-6	0	X			0	15	2
118-1	0	0				6	2
118-2	0	X				12	3
118-3	0	X				11	4
118-4	0	X				8	1
118-5	X	0				10	4
118-6	very weak pattern					4	-
124-1	very weak pattern					1	-
124-2	very weak pattern					3	-
124-3	0	0				6	2
124-4	X	X				12	1
124-5	X	X				10	3
124-6	very weak pattern					2	-

X = Assigned with high probability
0 = Assignment less certain

Q = SiO_2(α-quartz)

C = $CaCO_3$(calcite)

KAP = $(0.7NH_4H_2PO_4).(0.3\ KH_2PO_4)$

AS = $(NH_4)_2SO_4$

H = NaCl (halite)

Z = ZnO (zincite)

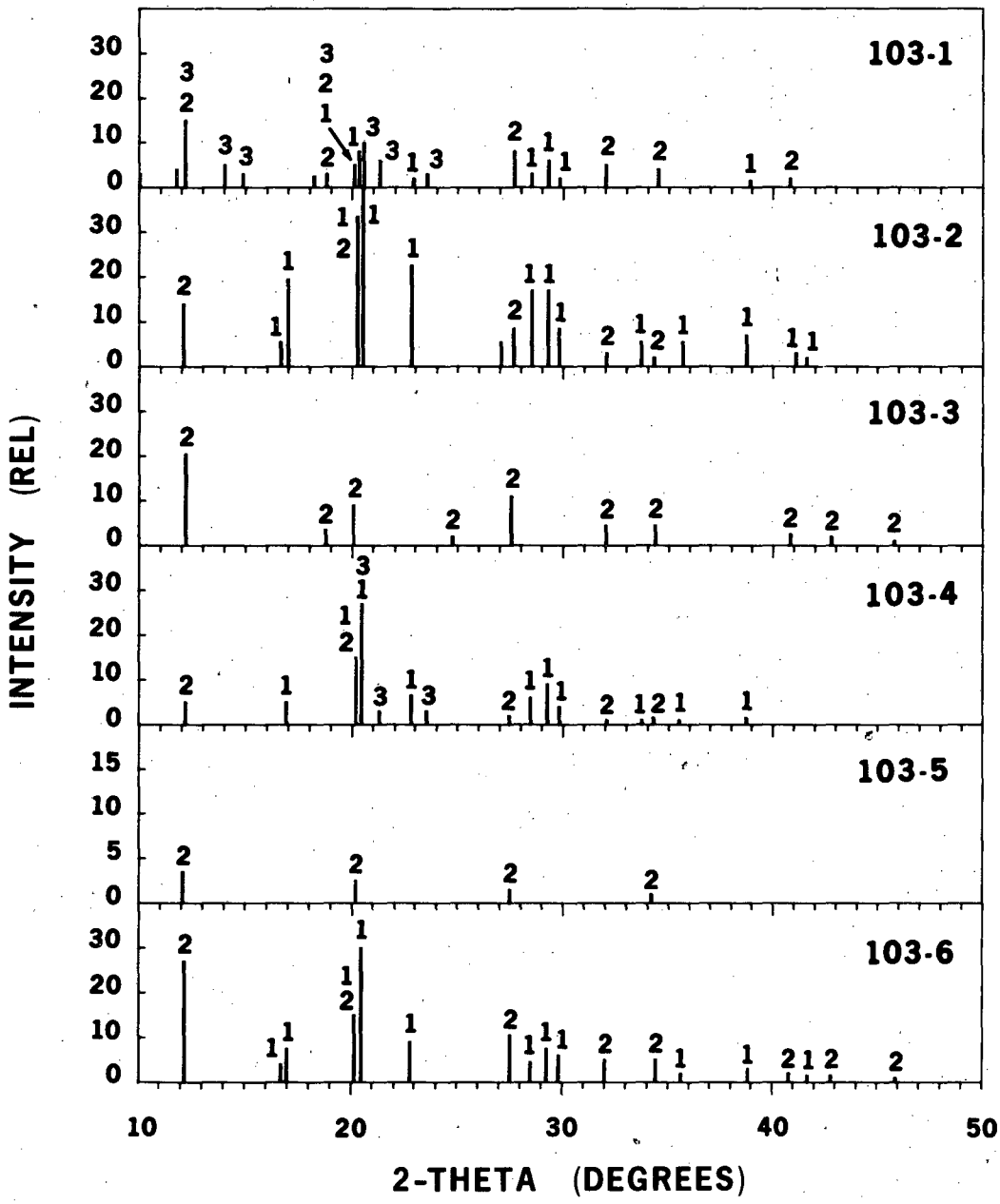
D = $(Ca,Mg)CO_3$ (dolomite)

Table 5 Concentrations of important elements (ng/m^3) and XPDFT results for simultaneous samples at four sites for the interval 1976/233/00. The coarse particle results for site 105 are not available. An asterisk (*) indicates that the element is stongly peaked in this interval.

SITE	103		105		118		124		AVERAGE[1] VALUES	
SIZE	F	C	F	C	F	C	F	C	F	C
MASS (μg/m^3)	67	75	99		53	48	44	25	32	22
Al	295	2788	452		120	1805	73	1556	130	900
Si	896	9778	1101		530	4651	381	3721	290	3300
P	-	54	54		-	243	-	214	10	30
S	8980	1020	11200		9900	480	8400	480	4000	340
Cl	600*	830	2020*		190	340	130	74	50	140
K	360	660	130		140	520	120	390	110	290
Ca	420	8090	180		200	8110	55	1400	75	1650
Fe	570	6770	590		200	1290	150	970	140	690
Cu	67	40	930*		2	2	4	3	9	4
Zn	370*	260	590*		64	30	50	20	50	28
Br	270	43	140		41	14	36	8	103	41
Pb	4190*	1080	12900*		300	42	180	26	560	140
Pb/Br	15.5		92.1		7.3		5.0		5.4	
XPDFT Results[2]	AS (Q) ALS (C)		AS ALS		ASH (Q) C		ASH weak pattern			

1) These are two month averages for site 120 taken from Dzubay (1979).

2) See Tables 3 and 4 for nomenclature.



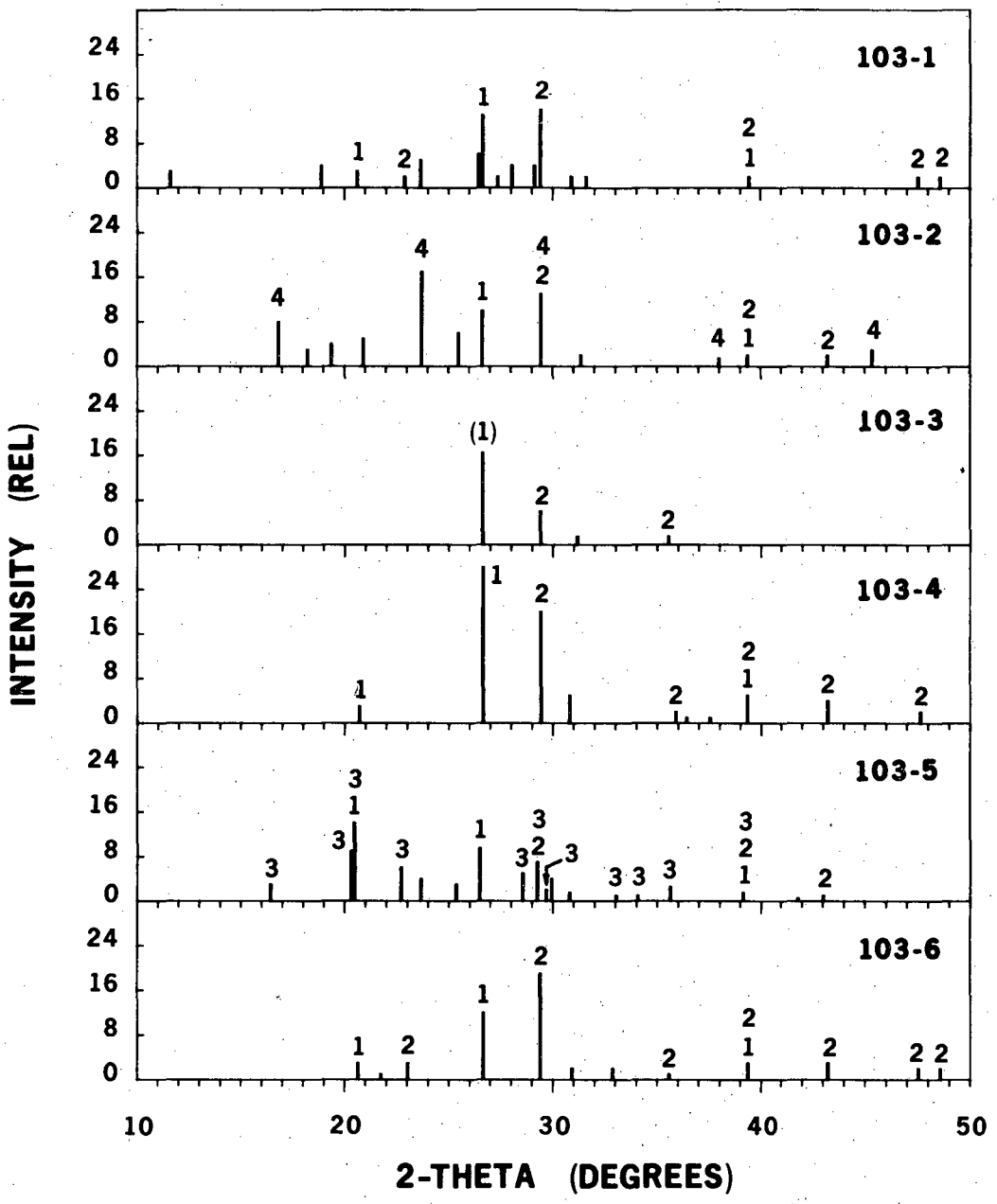
1=$(NH_4)_2SO_4$

2=$(NH_4)_2SO_4.PbSO_4$

3=$(NH_4)_2SO_4.ZnSO_4.6H_2O$

XBL 799-11779

Figure 1.



1=SiO_2

2=$CaCO_3$

3=$(NH_4)_2SO_4$

4=$(0.7NH_4H_2PO_4).(0.3KH_2PO_4)$

XBL 799-11778

Figure 2.

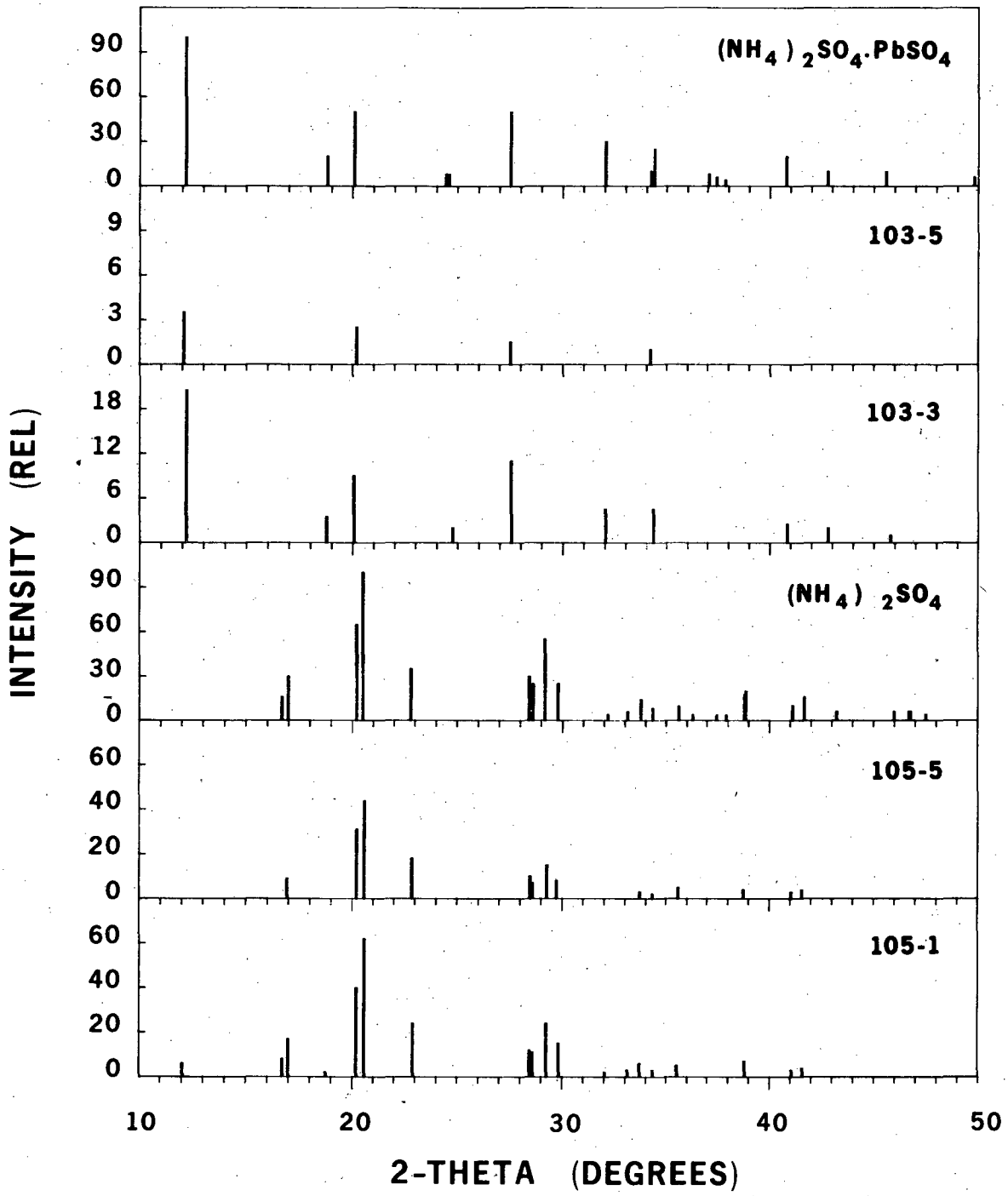

(NH4)2SO4.PbSO4
103-5
103-3
(NH4)2SO4
105-5
105-1
INTENSITY (REL)
2-THETA (DEGREES)
XBL 799-11780

Figure 3.

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